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⑤④ Fluoropolymer alloys, their preparation and application.

⑤⑦ This invention relates to fluoropolymer alloys made of melt fabricatable extra-high-molecular weight fluorinated ethylene-propylene copolymer (EHMW-FEP) and one or more other polymers. In fluoropolymer alloys made of EHMW-FEP and polytetrafluoroethylene, weight percentage of the former is 0.1-99.9% and the latter is 99.9-0.1%. The processes for preparing fluoropolymer alloys are blend of dried powder co-mill or wetted powder co-mill. Using the fluoropolymer alloys of this invention, various kinds of articles have been fabricated by melt compression or cold compaction and sintering. These properly fabricated articles show a great improvement in creep property and also a prolonged service life in comparison with those made from ordinary polytetrafluoroethylene.

## Fluoropolymer alloys,

## Their Preparation and Application

This invention relates to fluoropolymer alloys made of melt fabricatable extra-high-molecular weight fluorinated ethylene-propylene copolymer ( EHMW-FEP ) and one or more other polymers, their preparation and application.

The fluoropolymer alloys are new materials having different properties from original polymers of which they are made. It has become an important way to prepare new materials with a great variety of properties, because of its advantages of using available polymers, simple process, and short research period. It becomes of attracting interest recently Sato Kawa, plastics ( Japan ) ,32, 69 (1981). The fluoropolymer alloys which have been reported are limited to blending alloys based on polyvinylidene fluoride, as well as on polytetrafluoroethylene ( PTFE ) dispersion and fluorinated ethylene-propylene copolymer (FEP) dispersion (B.P. 935, 706, (1960); Japanese patent kokai 12521/62.

Polytetrafluoroethylene, common saying " King of plastics ", has excellent comprehensive properties. It has excellent thermal and chemical stability, and outstanding electrical insulation and anti-stick properties. But it could not be fabricated by melt processing, it can only be fabricated by cold compaction and then sintering. Its creep-resistance is also low. Therefore, its applications have been limited.

Fluorinated ethylene-propylene copolymer having good

creep-resistance is copolymer of tetrafluoroethylene and hexafluoro-propylene, it can be melt fabricated due to the presence of trifluoromethyl in the copolymer chain. The chemical inertness and outstanding electrical insulating properties of the copolymer are similar to polytetrafluoroethylene, but its thermal stability is not so excellent as PTFE, it can only withstand temperature up to 200 C, and its cost is higher than that of PTFE.

The purpose of present invention is to prepare a fluorine-containing material with more perfect properties through blending PTFE and FEP, and obtaining a polymer alloy in enhancing excellent properties and overcoming drawbacks of the two original polymers.

There are processes for preparing polymer alloy made of polytetrafluoroethylene and fluorinated ethylene-propylene copolymer in B.P. 935, 706 (1960) and Japanese patent kokai 12521/62, by using co-precipitation of these two fluoropolymer dispersions. The process is complicated, and the cost increased. Mechanical properties of the fluoropolymer alloy is worse than that of PTFE and FEP, for example their tensile strength is much lower than that of the two original polymers and only 142-213 Kg/cm<sup>2</sup> under room temperature.

An important problem is to match the polytetrafluoroethylene with fluorinated ethylene-propylene copolymer in order to get a good fluoropolymer alloy made of PTFE and FEP. These two raw fluoropolymers have

different processing temperatures and different thermal stability. Temperature of melt compression molding of FEP is about  $310^{\circ}\text{C}$ , but sintering temperature after cold compaction of PTFE is about  $380^{\circ}\text{C}$ . The decomposition rate of FEP is much higher than that of PTFE at  $380^{\circ}\text{C}$ . Particularly, when FEP resin having carboxyl end group is prepared by copolymerization using persulfates as initiator, it must be roasted at  $380^{\circ}\text{C}$  in order to stabilize the end group. However, FEP resins become "bread ruck", after roasted, and could not be blended with PTFE powder.

Another important problem is the blend process of preparing a polymer alloy made of PTFE and FEP. In general blending polymers can be carried out by solution blend method, melt blend or dispersion co-precipitate blend method. As there is no any solvent found for PTFE and FEP, they could not be carried out by solution blend. They could not be carried out by melt blend also, because PTFE could not be melt processed. Therefore, the dispersion co-precipitating blend has been the only way used in B.P. 935, 706 and Japanese patent kokai 12521/62, although the cost of the polymer alloy should be high, by using expensive fluorine-containing emulsifier in preparing dispersion of PTFE and FEP. Besides, the process of co-precipitating blend is rather complicate.

One of the feature of the present invention is to provide a fluoropolymer alloy made of extra-high-molecular weight fluorinated ethylene-propylene copolymer as its

chief component. EHMW-FEP is characterised by having melt processing property and matching with PTFE.

The second feature of the present invention is to provide a blend process of dried powder co-mill or wetted powder co-mill for preparing the fluoropolymer alloy.

The third feature of the present invention is to provide a fluoropolymer alloy which is characterised by having melt fabrication property like FEP and cold compression and sintering property like PTFE, and having the excellent properties possessed by both PTFE and FEP.

The fourth feature of the present invention is to provide a series of fluoropolymer alloy made of EHMW-FEP as their chief component, and at least one other polymer ( including fluorine-containing or common polymers ).

According to the present invention, the EHMW-FEP is a molding powder which can be melt fabricated, with melt viscosity of  $1 \times 10^6$  poises or more, melt flow index less than 0.8 gram/10min., 12 to 30% by weight of hexafluoropropylene, weight-average molecular weight of  $2 \times 10^5$  or more and tensile strength of 270 Kg/cm<sup>2</sup> or more under room temperature.

The process for preparing extra-high-molecular weight fluorinated ethylene-propylene copolymer which can be melt fabricated is a solution precipitating polymerization with liquid hexafluoropropylene as a solvent, including through raising the concentrations of monomers in reaction area by increasing amount of monomers in a autoclave and increasing

amount of tetrafluoroethylene in the initial monomer mixture of tetrafluoroethylene and hexafluoropropylene, through reducing the concentration of free radical in polymerization area and thus reducing termination possibility of the copolymer chain by reducing amount of initiator diisopropyl peroxydicarbonate used. All these conditions are advantageous to growing up the copolymer chain and to preparing much high molecular weight copolymer. Polymerization conditions are as follows: 1) charging 0.2-0.5 gram/ml of a mixture of tetrafluoroethylene and hexafluoropropylene in a autoclave, 2) tetrafluoroethylene weight ratio in initial monomer mixture of tetrafluoroethylene and hexafluoropropylene is 11-50%, 3) initiator diisopropyl peroxydicarbonate ( IPP ) is 0.001 to 0.05% equivalents based on monomers, 4) weight ratio between water and monomer is 3/1 to 1/1; polymerization temperature, 40-80°C; polymerization pressure, 20-30 Kg/cm<sup>2</sup>; polymerization time, 1-5 hours a batch.

According to the present invention, the PTFE used is a commercial resin, including resins prepared by suspension or dispersion polymerization, and has tensile strength more than 270 Kg/cm<sup>2</sup> under room temperature.

According to the present invention, the other commercial polymers, such as polychlorotrifluoroethylene, polyvinylidene fluoride, tetrafluoroethylene-ethylene copolymer, polyethylene, polypropylene, polysulfone, polyimide, polycarbonate, polyphenylene oxide, poly(phenylene sulfide ) et al, can used to prepare fluoro-

polymer alloy together with extra-high-molecular weight fluorinated ethylene-propylene copolymer.

A given weight ratio of EHMW-FEP and one or more other polymers as described above, have been ground by mill separately, and then mixed and ground again until the two or more phases were homogeneously mixed. The mixture is screened by a 40-80 mesh and ready for processing.

The mixing and grinding process of two or more polymers, may be mixed and ground either in dried powder form or wet powder form. During wet power mixing and grinding, the polymers are moistened by water, ethyl alcohol, ethyl acetate or a mixture of these solvents. When the mixing is finished, the mixture of polymers must be dried, and then screened.

In the fluoropolymer alloy made of EHMW-FEP and PTFE, the weight of EHMW-FEP is 0.1-99.9% and the weight of PTFE is 99.9-0.1%. In preferred embodiment the weight ratios have 0.1-60% of EHMW-FEP and 40-99.9% of PTFE.

The fluoropolymer alloys made of EHMW-FEP and PTFE can be melt pressing into articles under temperature of 300-350° C and pressure of 50-200Kg/cm<sup>2</sup> like FEP. They can also be cold compressed under pressure of 50-200 Kg/cm<sup>2</sup> and then sintering under temperature of 300-390° C like PTFE.

The temperatures of melt pressing or sintering fluoropolymer alloys described above depend on the amount of PTFE in them. The more the amount of PTFE, the higher the temperature.

The fluoropolymer alloys made of EHMW-FEP and PTFE of present invention have not only creep-resistance like FEP, but also high tensile strength under high temperature like PTFE. It exhibits tensile strength of 200-400 Kg/cm<sup>2</sup> and elongation of 300-700% under room temperature, and correspondingly 50-200 Kg/cm<sup>2</sup> and 300-700% under 200° C.

extra-high-molecular weight fluorinated ethylene-propylene copolymer have a good compatibility with polytetrafluoroethylene in the fluoropolymer alloys described above. Fluoropolymer alloy, e.g., made of 10% of EHMW-FEP and 90% of PTFE, has nearly only one peak of melting and one peak of crystallizing in its DSC spectrum.

All kind of the fluoropolymer alloys described above can be reinforced and improved by adding glass fiber, graphite, molybdenum disulfide, carbon and various metal powders.

The fluoropolymer alloys made of EHMW-FEP and PTFE of present invention are a kind of materials having excellent thermal stability, chemical inertness and outstanding electrical insulating properties. Taking this kind of fluoropolymer alloys as material, various diaphragm, seals, lining valves, lining pipes, lining pump, various components of pump, such as shell, wheel, wind wrap wire etc. can be fabricated. The articles made of fluoropolymer alloys have better creep-resistance than that of PTFE and consequently have a rather long operating life.

The fluoropolymer alloys described above can be used in power coating by either static electricity method or



flow-bed method, and can also be fabricated into complex articles using ram-extruding a paste consists of fluoropolymer alloy and petroleum ether or kerosene.

The invention is more specifically described and explained by means of the following examples which, however, are not intended to be limiting. In the examples all parts and percentages are by weight except as otherwise noted.

#### Example 1

20 grams of EHMW-FEP with melt flow index of 0 gram/10min., and 180 grams PTFE have successively been moistened by a mixture of ethyl alcohol and ethyl acetate, milled, filtered, dried and passed through a 40 mesh screen. The resulting powder is cold compressed into a 2 mm thick sheet under pressure of 80 Kg/cm<sup>2</sup>, and sintered in a oven for 1 hour at 350°C. After cooling, its tensile strength is 277 Kg/cm<sup>2</sup> under room temperature.

#### Example 2

Mixing EHMW-FEP with PTFE in weight ratio of 1/9, 1/3, 1/1, 3/1 and 9/1 respectively, the resulting mixtures are milled to pass through 40 mesh screen, cold compressed under 80 Kg/cm<sup>2</sup> and sintering separately. The properties of the resulting fluoropolymer alloys are shown in Table 1.

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Table 1. Physical properties of alloys made of EHMW-FEP/PTFE

| Composition (EHMW-FEP/PTFE)  | 1/0 | 9/1 | 3/1 | 1/1 | 1/3     | 1/9     | 0/1 |
|--|-----|-----|-----|-----|---------|---------|-----|
| sintering temp. ( $^{\circ}\text{C}$ )                                 | 300 | 300 | 300 | 320 | 340-365 | 340-365 | 365 |
| room tensile strength<br>temp. ( $\text{Kg}/\text{cm}^2$ )             | 265 | 210 | 250 | 290 | 260     | 280     | 320 |
| elongation (%)   | 330 | 310 | 370 | 500 | 520     | 520     | 650 |
| 200 $^{\circ}\text{C}$ tensile strength<br>( $\text{Kg}/\text{cm}^2$ ) | 46  | 87  | 84  | 82  | 89      | 104     | 89  |
| elongation (%)   | 340 | 340 | 500 | 450 | 500     | 680     | 480 |

### Example 3

Mixing EHMW-FEP with tetrafluoroethylene-ethylene copolymer (F40) in weight ratio showed in Table 2 by blending dried powder or wetted powder, the resulting fluoropolymer alloys are fabricated by cold compression under pressure of 70-150  $\text{Kg}/\text{cm}^2$  and then sintering, or by melt pressing.

Table 2. Physical properties of alloys made of EHMW-FEP and F40

| Composition<br>(EHMW-FEP/F40)             | 1/0  | 99/1 | 9/13/1 | 1/1  | 1/3  | 1/9  | 1/99 | 0/1       |
|---|------|------|--------|------|------|------|------|-----------|
| fabrication temp. (°C)                    | 310- | 300- | 300-   | 300- | 300- | 300- | 300- | 280- 280- |
| tensile strength<br>(Kg/cm <sup>2</sup> ) | 300  | 310  | 315    | 320  | 325  | 330  | 340  | 350 400   |
| elongation (%)                            | 300  | 300  | 280    | 260  | 200  | 150  | 100  | 100 100   |

#### Example 4

A mixture of 40 grams of EHMW-FEP, 40 grams of PTFE and 10 grams of polysulfone, is moistened with acetone, mixed homogeneously by high speed stirring, milled, dried, 40 mesh screened, cold compressed under 80 Kg/cm<sup>2</sup> and then sintering for one hour at 320° C. The hardness (Rockwell) of the fluoropolymer alloy obtained is D50.

#### Example 5

Mixing EHMW-FEP with polychlorotrifluoroethylene (CTFE) in weight ratio showed in Table 3 by blending dried powder or wetted powder, the resulting fluoropolymer alloys

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are fabricated by cold compression under pressure of 70-150 Kg/cm<sup>2</sup> and then sintering, or by melt pressing.

Table 3. Physical properties of alloys made of EHMW-FEP and CTFE

| Composition<br>(EHMW-FEP/CTFE)            | 1/0  | 99/1 | 9/1  | 3/1  | 1/1  | 1/3  | 1/9  | 1/99 | 0/1  |
|---|------|------|------|------|------|------|------|------|------|
| fabrication temp. (°C)                    | 310- | 310- | 300- | 270- | 250- | 250- | 250- | 250- | 250- |
|   | 380  | 330  | 330  | 300  | 300  | 300  | 300  | 300  | 320  |
| tensile strength<br>(Kg/cm <sup>2</sup> ) | 300  | 280  | 200  | 220  | 300  | 305  | 320  | 300  | 350  |
| elongation (%)                            | 350  | 300  | 40   | 100  | 250  | 180  | 200  | 150  | 150  |

#### Example 6

Mixing EHMW-FEP with polyvinylidene fluoride (PVDF) in weight ratio showed in Table 4 by blending dried powder or wetted powder (including using diisobutyl acetone as a moistener), the resulting fluoropolymer alloys are fabricated by cold compression under pressure of 70-150 Kg/cm<sup>2</sup> and then sintering, or by melt pressing.

Table 4. Physical properties of alloys made of EHMW-FEP and PVDF

| Composition<br>(EHMW-FEP/PVDF)            | 1/0  | 99/1 | 9/1  | 3/1  | 1/1  | 1/3  | 1/9  | 1/99 | 0/1  |
|---|------|------|------|------|------|------|------|------|------|
| fabrication temp. (°C)                    | 310- | 280- | 280- | 230- | 250- | 240- | 220- | 200- | 200- |
|   | 380  | 320  | 330  | 330  | 330  | 300  | 230  | 250  | 250  |
| tensile strength<br>(Kg/cm <sup>2</sup> ) | 310  | 330  | 350  | 300  | 300  | 350  | 420  | 450  | 500  |
| elongation (%)                            | 320  | 250  | 200  | 150  | 150  | 100  | 60   | 60   | 50   |

#### Example 7

Mixing EHMW-FEP with polysulfone (PS) in weight ratio showed in Table 5 by blending dried powder or wetted powder (including using chloroform as a solvent), the resulting fluoropolymer alloys are fabricated by melt compression under pressure of 70-150 Kg/cm<sup>2</sup>.

Table 5. Physical properties of alloys made of EHMW-FEP and PS

| Composition<br>(EHMW-FEP/PS)                 | 1/0  | 99/1 | 9/1  | 3/1  | 1/1  | 1/3  | 1/9  | 1/99 | 0/1  |
|--|------|------|------|------|------|------|------|------|------|
| fabrication<br>temp. (°C)                    | 310- | 280- | 250- | 220- | 250- | 250- | 270- | 200- | 200- |
|  | 380  | 320  | 310  | 300  | 290  | 290  | 280  | 270  | 280  |
| tensile<br>strength<br>(Kg/cm <sup>2</sup> ) | 300  | 270  | 250  | 220  | 200  | 250  | 360  | 700  | 800  |
| elongation<br>(%)                            | 320  | 250  | 200  | 100  | 4    | 5    | 5    | 40   | 50   |

#### Example 8

Mixing EHMW-FEP with polyethylene (PE) in weight ratio showed in Table 6 by blending dried powder or wetted powder (including using xylene as a solvent), the resulting fluoropolymer alloys are fabricated by melt compression under pressure of 70-150 Kg/cm<sup>2</sup>.

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Table 6. Physical properties of alloys made of EHMW-FEP and PE

| Composition<br>(EHMW-FEP/PE)              | 1/0  | 99/1 | 9/1  | 3/1  | 1/1  | 1/3  | 1/9  | 1/99 | 0/1  |
|---|------|------|------|------|------|------|------|------|------|
| fabrication temp. (°C)                    | 310- | 280- | 250- | 200- | 170- | 150- | 160- | 150- | 150- |
|   | 380  | 350  | 300  | 300  | 250  | 200  | 170  | 170  | 200  |
| tensile strength<br>(Kg/cm <sup>2</sup> ) | 300  | 280  | 250  | 180  | 100  | 150  | 190  | 200  | 200  |
| elongation 1%                             | 350  | 300  | 200  | 100  | 50   | 400  | 600  | 210  | 250  |

#### Example 9

Mixing EHMW-FEP with polypropylene (pp) in weight ratio showed in Table 7 by blending dried powder or wetted powder (including using decalin as a solvent), the resulting fluoropolymer alloys are fabricated by melt compression under pressure of 70-150 Kg/cm<sup>2</sup>.

Table 7. Physical properties of alloys made of EHMW-FEP and PP

| Composition<br>(EHMW-FEP/PP)              | 1/0  | 99/1 | 9/1  | 3/1  | 1/1  | 1/3  | 1/9  | 1/99 | 0/1  |
|---|------|------|------|------|------|------|------|------|------|
| fabrication<br>temp. (°C)                 | 310- | 300- | 280- | 250- | 230- | 220- | 220- | 220- | 230- |
|   | 380  | 330  | 320  | 300  | 300  | 280  | 250  | 260  | 300  |
| tensile strength<br>(Kg/cm <sup>2</sup> ) | 310  | 300  | 280  | 200  | 180  | 200  | 240  | 310  | 350  |
| elongation (%)                            | 340  | 300  | 350  | 200  | 300  | 350  | 500  | 250  | 200  |

#### Example 10

Mixing EHMW-FEP with polycarbonate (PC) in weight ratio showed in Table 8 by blending dried powder or wetted powder (including using chloroform as a solvent), the resulting fluoropolymer alloys are fabricated by melt compression under pressure of 70-150 Kg/cm<sup>2</sup>.



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Table 8. Physical properties of alloys made of EHMW-FEP and PC

| Composition<br>(EHMW-FEP/PC)              | 1/0  | 99/1 | 9/1  | 3/1  | 1/1  | 1/3  | 1/9  | 1/99 | 0/1  |
|---|------|------|------|------|------|------|------|------|------|
| fabrication<br>temp. (°C)                 | 310- | 300- | 290- | 290- | 280- | 280- | 280- | 250- | 220- |
|   | 380  | 350  | 340  | 330  | 320  | 310  | 310  | 320  | 350  |
| tensile strength<br>(Kg/cm <sup>2</sup> ) | 310  | 300  | 280  | 260  | 200  | 300  | 360  | 550  | 700  |
| elongation (%)                            | 350  | 300  | 200  | 100  | 50   | 10   | 5    | 80   | 100  |

#### Example 11

Mixing EHMW-FEP with polyphenylene oxide (ppo) in weight ratio showed in Table 9 by blending dried powder or wetted powder (including using chloroform as a solvent), the resulting fluoropolymer alloys are fabricated by melt compression under pressure of 70-150 Kg/cm<sup>2</sup>.

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Table 9. Physical properties of alloys made of EHMW-FEP and PPO

| Composition<br>(EHMW-FEP/PPO)             | 1/0  | 99/1 | 9/1  | 3/1  | 1/1  | 1/3  | 1/9  | 1/99 | 0/1  |
|---|------|------|------|------|------|------|------|------|------|
| fabrication<br>temp. (°C)                 | 310- | 300- | 300- | 300- | 300- | 300- | 305- | 300- | 300- |
|   | 380  | 320  | 320  | 320  | 320  | 320  | 310  | 320  | 350  |
| tensile strength<br>(Kg/cm <sup>2</sup> ) | 305  | 280  | 250  | 200  | 150  | 50   | 110  | 250  | 650  |
| elongation (%)                            | 330  | 250  | 200  | 100  | 10   | 4    | 5    | 40   | 50   |

#### Example 12

Mixing EHMW-FEP with polyphenylene sulfide (PPS) in weight ratio showed in Table 10 by blending dried or wetted powder, the resulting fluoropolymer alloys are fabricated by melt compression under pressure of 70-150 Kg/cm<sup>2</sup>.

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Table 10. Physical properties of alloys made of EHMW-FEP and PPS

| Composition<br>(EHMW-FEP/PPS)                   | 1/0  | 99/1 | 9/1  | 3/1  | 1/1  | 1/3  | 1/9  | 1/99 | 0/1  |
|---|------|------|------|------|------|------|------|------|------|
| fabrication<br>temp. ( $^{\circ}\text{C}$ )     | 310- | 300- | 300- | 300- | 300- | 300- | 300- | 300- | 290- |
| tensile strength<br>( $\text{Kg}/\text{cm}^2$ ) | 300  | 290  | 280  | 250  | 200  | 300  | 400  | 850  | 900  |
| elongation (%)                                  | 320. | 300  | 250  | 200  | 100  | 50   | 5    | 15   | 10   |

#### Example 13

Mixing EHMW-FEP with polyimide (PI) in weight ratio showed in Table 11 by blending dried powder or wetted powder, the resulting fluoropolymer alloys are fabricated by melt compression under pressure of  $70\text{--}150 \text{ Kg}/\text{cm}^2$  or cold compaction under pressure of  $70\text{--}150 \text{ Kg}/\text{cm}^2$  and sintering.

Table 11. Physical properties of alloys made of EHMW-FEP and PI

| Composition<br>(EHMW-FEP-PI)              | 1/0  | 99/1 | 9/1  | 3/1  | 1/1  | 1/3  | 1/9  | 1/99 | 0/1  |
|---|------|------|------|------|------|------|------|------|------|
| fabrication<br>temp. (°C)                 | 310- | 300- | 300- | 300- | 300- | 300- | 310- | 250- | 150- |
| tensile strength<br>(Kg/cm <sup>2</sup> ) | 320  | 310  | 300  | 250  | 200  | 300  | 400  | 800  | 900  |
| elongation (%)                            | 330  | 300  | 280  | 250  | 100  | 80   | 50   | 10   | 5    |

#### Example 14

Mixing 10 grams of EHMW-FEP with 90 grams molding powder or dispersion powder of PTFE, and then the resulting mixture was milled, 40 mesh screened. The resulting dried powder of fluoropolymer alloy are moistened by 200E gasoline, cold compressed and sintered. This fluoropolymer alloy product can be used for lining valves and pipes.

#### Example 15

Mixing 40 grams of fluoropolymer alloy made of EHMW-FEP and PTFE with glass fiber in its weight ratio of 10%, 20% and 30% respectively. The resulting mixture are cold compressed under pressure of 80 Kg/cm<sup>2</sup> and sintered for 2 hours at 320°C separatly. The date of tensile strength of

these reinforced fluoropolymer alloy are 250, 220 and 150 Kg/cm<sup>2</sup>, respectively, under room temperature.

#### Example 16

Mixing fluoropolymer alloy made of 50 grams of EHMW-FEP and 50 grams of PTFE with glass fiber in its weight ratio of 20% and graphite in its weight ratio of 3%, the resulting mixture is milled to pass through 40 mesh screen, cold compressed under pressure of 80 Kg/cm<sup>2</sup> and then sintered for 2 hours at 320° C. The tensile strength, elongation and hardness (Rockwell) of the reinforced fluoropolymers alloys are 150 Kg/cm<sup>2</sup>, 220% and 58, respectively.

#### Example 17

Process for preparing extra-high-molecular weight fluorinated ethylene-propylene copolymer, e.g. in a stainless-steel autoclave having a capacity of 130 liters are charged 60 liters of deionized water, 45 Kg of initial monomers containing hexafluoropropylene weight ratio of 86.6%. The contents are heated to 55-57°C with a pressure of 22.0 Kg/cm<sup>2</sup>, then 25 ml of diisopropyl peroxydicarbonate are added. The copolymerization is carried on for three hours. 7.5 Kg of dried copolymer powder having a hexafluoropropylene weight ratio of 14.5%, a melt viscosity of  $1.8 \times 10^6$  poises and a melt flow index of 0.3 g/10 min could be obtained. A sample of the copolymer powder is molded into sheet with a thickness of 2 mm at 310°C, which shows the tensile strength 290 Kg/cm<sup>2</sup> elongation 320%; and flex fatigue life more than  $2 \times 10^5$  cycle under room

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temperature.

What we claim is:

1. Fluoropolymer alloys, which comprises the melt fabricatable extra-high-molecular weight fluorinated ethylene-propylene and one or more other polymers, such as polytetrafluoroethylene, polychlorotrifluoroethylene, polyvinylidene fluoride, tetrafluoroethylene-ethylene copolymer, polysulfone, polyethylene, polypropylene, polyimide, polycarbonate, polyphenylene oxide or polyphenylene sulfide.

2. The fluoropolymer alloys as claimed in claim 1, wherein the molding powder is extra-high-molecular weight fluorinated ethylene-propylene copolymer which can be melt fabricated, with 12-30% by weight of hexafluoropropylene, weight-average molecular weight of over  $2 \times 10^5$ , melt viscosity of more than  $1 \times 10^6$  poises, melt flow index less than 0.8 gram/10 minute.

3. The fluoropolymer alloys as claimed in claim 1, which comprises extra-high-molecular weight fluorinated ethylene-propylene copolymer and polytetrafluoroethylene in any weight ratio.

4. The fluoropolymer alloys as claimed in claim 3 characterised by having weight ratio of 0.1-60% extra-high-molecular weight fluorinated ethylene-propylene copolymer and 99.9-40% polytetrafluoroethylene.

5. The fluoropolymer alloys as claimed in claim 1, 2, 3 or 4, wherein glass fiber, graphite, molybdenum disulfide, carbon or metal powder may be added.

6. A process for preparing the fluoropolymer alloys as claimed in claim 1, either dried powder co-mill or wetted powder CO-mill.

7. The process of dried powder co-mill for preparing fluoropolymer alloys as claimed in claim 6 characterised by comprising milling extra-high-molecular weight fluorinated ethylene-propylene copolymer and one or more other polymers, such as polytetrafluoroethylene, polychlorotrifluoroethylene, polyvinylidene fluoride, tetrafluoroethylene-ethylene copolymer, polyethylene, polypropylene, polysulfone, polyimide, polycarbonate, polyphenylene oxide or polyphenylene sulfide separately, and then mixing the polymers in a given weight ratio and milling the mixture again until homogeneously, passing through 40 mesh screen.

8. The process of wetted powder co-mill for preparing fluoropolymer alloys as claimed in claim 6 characterised comprising by moistening a given amount of extra-high-molecular weight fluorinated ethylene-propylene copolymer and at least one or more other polymers, such as polytetrafluoroethylene, polychlorotrifluoroethylene, polyvinylidene fluoride, tetrafluoroethylene-ethylene copolymer, polyethylene, polypropylene, polysulfone, polyimide, polycarbonate, polyphenylene oxide or polyphenylene sulfide by water, ethyl alcohol, ethyl acetate or a mixed solvent of them and then milling and blending until homogeneously, filtering, drying, finally 40 mesh screening.

9. The fluoropolymer alloys as claimed in claim 1 or



6, which can be fabricated by melt compression, cold compaction and sintering, powder coating, powder coating of flow-bed, or ram-extruding of paste consisting of dried powder and moistener.

10. The process of melt compression for fluoropolymer alloys as claimed in claim 9 characterised by temperature of 300-350 C and pressure of 50-200 Kg/cm<sup>2</sup>.

11. The process of cold compaction and sintering for fluoropolymer alloys as claimed in claim 9 characterised by cold compressing under pressure of 50-200 Kg/cm<sup>2</sup> and sintering under temperature of 300-390° C.

12. The process of ram-extruding of paste consisting of dried powder and moistener for fluoropolymer alloys as claimed in claim 9 characterised by using petroleum ether of kerosene as a moistener.

13. The fluoropolymer alloys claimed in claim 1,2,3,4 or 5, which may be fabricated into various articles such as diaphragms, seals, lining valves, lining pipes, lining pumps, shell and wheel of corrosive-resistance pump, wind-wrap wire, they exhibit excellent thermal stability, chemical inertness and outstanding electrical insulating properties.

14. The process for preparing extra-high-molecular weight fluorinated ethylene-propylene copolymer suitable for melt fabrication as claimed in claim 1 or 2, which comprises a solution precipitation polymerization using liquid hexafluoropropylene as a solvent, which are

characterised by charging 0.2-0.5 g of tetrafluoroethylene and hexafluoropropylene per 1 ml autoclave capacity into a autoclave, and the monomer mixture of tetrafluoroethylene and hexafluoropropylene containing 11-50% by weight of tetrafluoroethylene, the weight ratio between water and monomers in 3:1 to 1:1, equivalents of initiator diisopropyl peroxy dicarbonate based on monomers being, 0.001 to 0.05% the polymerization pressure of 20-30 Kg/cm<sup>2</sup>, polymerization temperature of 40 to 80°C, and polymerization time of 1-5 hours a batch.



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(54) Fluoropolymer alloys, their preparation and application.

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(57) This invention relates to fluoropolymer alloys made of melt fabricatable extra-high-molecular weight fluorinated ethylene-propylene copolymer (EHMW-FEP) and one or more other polymers. In fluoropolymer alloys made of EHMW-FEP and polytetrafluoroethylene, weight percentage of the former is 0.1-99.9% and the latter is 99.9-0.1%. The processes for preparing fluoropolymer alloys are blend of dried powder co-mill or wetted powder co-mill. Using the fluoropolymer alloys of this invention, various kinds of articles have been fabricated by melt compression or cold compaction and sintering. These properly fabricated articles show a great improvement in creep property and also a prolonged service life in comparison with those made from

ordinary Polytetrafluoroethylene.



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# EUROPEAN SEARCH REPORT

Application Number

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| DOCUMENTS CONSIDERED TO BE RELEVANT  |   |  |  |
|--|---|--|--|
| Category   | Citation of document with indication, where appropriate, of relevant passages   | Relevant to claim                              | CLASSIFICATION OF THE APPLICATION (Int. Cl.4)                        |
| X  | EP-A-0 088 414 (DAIKIN KOGYO)<br>* Abstract; page 1, line 24 - page 2, line 18; page 4, lines 4-12; page 4, line 20 - page 5, line 20; page 7, lines 19-26 *<br>--- | 1-3  | C 08 L 27/18<br>C 08 L 101/00 //<br>(C 08 L 27/18<br>C 08 L 101:00 ) |
| X  | EP-A-0 106 764 (SOCIETE CHIMIQUE DE CHARBONNAGES)<br>* Page 2, lines 15-34; claim 9 *<br>---  | 1-2,10   |  |
| X  | GB-A-2 144 761 (NIPPON PISTON RING)<br>* Claim *<br>---   | 1,2  |  |
| X  | GB-A- 935 706 (E.I. DU PONT DE NEMOURS)<br>* Claim 1 *<br>-----   | 1-4  |  |
|  |   |  | TECHNICAL FIELDS SEARCHED (Int. Cl.4)                                |
|  |   |  | C 08 L<br>C 08 F   |
| The present search report has been drawn up for all claims   |   |  |  |
| Place of search<br>THE HAGUE   |   | Date of completion of the search<br>19-12-1989 | Examiner<br>GOOVAERTS R.E.   |
| CATEGORY OF CITED DOCUMENTS  |   |  |  |
| <p>X : particularly relevant if taken alone<br/>Y : particularly relevant if combined with another document of the same category<br/>A : technological background<br/>O : non-written disclosure<br/>P : intermediate document</p> <p>T : theory or principle underlying the invention<br/>E : earlier patent document, but published on, or after the filing date<br/>D : document cited in the application<br/>L : document cited for other reasons<br/>-----<br/>&amp; : member of the same patent family, corresponding document</p> |   |  |  |